

Acetyl nitrate nitrations in [bmpy][N(Tf)₂] and [bmpy][OTf], and the recycling of ionic liquids†‡

Emilie Dal and N. Llewellyn Lancaster*

Department of Chemistry, King's College London, Strand, London, WC2R 2LS, UK.
E-mail: llewellyn.lancaster@kcl.ac.uk

Received 11th November 2004, Accepted 10th December 2004
First published as an Advance Article on the web 24th January 2005

In this work we have examined the nitration by acetyl nitrate of a range of activated and deactivated aromatic substrates in two ionic liquids and compared the results to the same reaction in dichloromethane. Both ionic liquids are stable to the reaction conditions, and in both ionic liquids the yields of reaction are higher after unit time than the same reactions in dichloromethane, although the regioselectivity is little affected by solvent choice. This result gives further support to the suggestion that in the ionic liquid, acetyl nitrate dissociates to give the nitronium ion, and that this is the effective nitrating agent here. However, it is shown that [bmpy][N(Tf)₂] is a better solvent for aromatic nitration than [bmpy][OTf]. This is due to the ease of formation of nitronium ion in the former ionic liquid, and is consistent with the fact that [bmpy][N(Tf)₂] is a weaker hydrogen bond acceptor solvent than [bmpy][OTf]. Finally, a method by which [bmpy][N(Tf)₂] may be recovered and reused for aromatic nitration has been demonstrated.

Introduction

The use of ionic liquids as alternative reaction media for organic chemistry is an active and important area of current research.^{2,3} Ionic liquids are attractive because they have certain “green” properties, including near zero vapour pressure. Additionally, it is possible, by choice of cation and anion, to tune the solvent properties of the ionic liquid,⁴ for example. The potential to design a solvent for a specific reaction (or reaction class) provides a contrast to what is possible with molecular solvents where choice is limited.

Aromatic nitration is a reaction of synthetic and industrial importance, despite the fact that it is a notoriously “ungreen” reaction. One particular problem is that conventional aromatic nitration makes use of the mixed acid system, in which nitric acid is used in conjunction with an excess of concentrated sulfuric acid. For this reason, a range of alternative systems for aromatic nitrations which do not require sulfuric acid have been developed in recent years. These include the use of clays^{5,6} or zeolites^{7–9} as solid supports; lanthanide^{10,11} and transition^{12,13} metal catalysts or employing perfluorocarbons as solvents.¹⁴

Nitration has also long been of academic interest, having been used as a tool to increase our understanding of organic reaction mechanisms, particularly electrophilic substitution.¹⁵ The consequence of this is that the mechanisms of aromatic nitrations are well known, and it is possible to make a comparison between systems. The twin aims of this work are to study aromatic nitrations as models of electrophilic substitution in ionic liquids (and to use this information to describe electrophilic substitutions in ionic liquids in general) whilst seeking an alternative, greener methodology for aromatic nitrations.

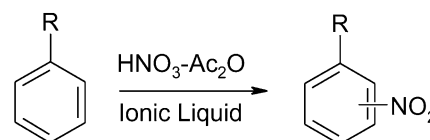
Aromatic nitrations in ionic liquids have already received some interest in recent years. The first published work was by Laali,¹⁶ using a variety of conventional nitrating agents. Complementary studies have since been made by us,¹ Earle¹⁷ and Qiao.¹⁸ During this period, Srinivasan and Rajagopal showed that iron nitrate can be used to nitrate phenols in ionic liquids.¹⁹ Despite these numerous studies, there have been only limited attempts to determine the mechanism of the reactions in the

ionic liquids, or the role of the solvent. This is in contrast to the study of other electrophilic substitutions in ionic liquids,²⁰ which the results of this work can also be compared against.

Our first paper discussed the importance of cation choice (showing that imidazolium-based cations were not stable to the reaction conditions) and demonstrated that an ionic liquid based on [bmpy]⁺ (where bmpy = 1-butyl-1-methylpyrrolidinium) was suitable. The effect of the anion was ignored in that work, although we did speculate on the fate of acetyl nitrate generated *in situ*.

Results and discussion

We now report the preliminary findings of the effect of the anion on aromatic nitrations by acetyl nitrate in ionic liquids as illustrated in Scheme 1.



Scheme 1 Acetyl nitrate nitrations in ionic liquids.

The nitrations were studied in two different ionic liquids, [bmpy][OTf] and [bmpy][N(Tf)₂], Fig. 1. § These ionic liquids were chosen because they can be prepared to a high standard of purity, are stable to the reaction conditions and have known (and different) solvent properties. For example, the Kamlet-Taft properties α , β and π^* have been determined for these solvents.^{21,22} It should be noted that the reactions are subtly different in this work than in the first paper. In the current work we used a larger volume of ionic liquid and less reagent, such that the ionic liquid is certainly acting as a solvent (and not as an additive) for the nitrating agent. This has had the effect of reducing yields after unit time (especially for the deactivated substrates), reflecting the reduced concentration of the nitrating agent.

† Aromatic nitrations in ionic liquids. Part 2.¹

‡ Electronic supplementary information (ESI) available: kinetic data for the nitration of toluene in dichloromethane and the nitration of chlorobenzene in [bmpy][N(Tf)₂] at 25 °C. See <http://www.rsc.org/suppdata/ob/b4/b417152g/>

§ In this work our intention has been to study anion effects. It has already been established that [bmpy]⁺ is a suitable cation for these reactions.¹ There is a limited choice of anions that, when combined with [bmpy]⁺, give room temperature ionic liquids which can be prepared such that they are free of organic and inorganic impurities.

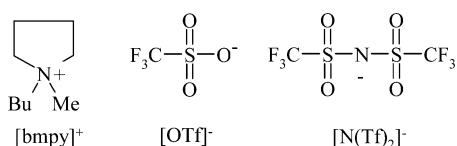


Fig. 1 Cations and anions used to prepare the ionic liquids used.

Effect of ionic liquid anions

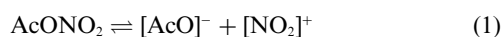
The nitration of a range of activated and deactivated aromatic substrates was studied in $[\text{bmpy}][\text{OTf}]$ and $[\text{bmpy}][\text{N(Tf)}_2]$ and a comparison was made with the same reaction in dichloromethane. The results are shown in Table 1.

There are a number of comparisons that can be made. The first is between the ionic liquids and dichloromethane. Although dichloromethane is a good solvent in which to conduct nitrations, only the activated substrates were nitrated. When deactivated substrates were employed, no reaction was observed. Additionally it can be noted that the yields of the nitroaromatics after 1 hour were lower in dichloromethane than under the same conditions in either ionic liquid. The regioselectivity of nitration (both of toluene and of anisole) was not much affected by the ionic liquid, and was comparable to that observed in dichloromethane.

As shown in earlier work, although acetyl nitrate is ineffective in the nitration of the deactivated haloaromatics under the conditions employed in dichloromethane, the reactions proceed in ionic liquids to give the nitroaromatic. The limit in nitration seems to be reached somewhere between 2-nitrotoluene and nitrobenzene. The former reacts slowly in $[\text{bmpy}][\text{N(Tf)}_2]$ over 24 hours, and gives a low yield in $[\text{bmpy}][\text{OTf}]$ over the same time period. Nitrobenzene barely reacts over 24 hours in either solvent.

This overview misses the subtler points about the nitration reactions in the ionic liquids. Whilst it is true that there is little between the yields and regioselectivities where the substrates are activated, the deactivated substrates reveal differences. It is striking that the nitration of halobenzenes in $[\text{bmpy}][\text{N(Tf)}_2]$ reaches *ca.* 60% yield in 1 hour, whilst in $[\text{bmpy}][\text{OTf}]$, the yield is less than 10%. Again, in the nitration of 2-nitrotoluene, the yield is an order of magnitude higher in $[\text{bmpy}][\text{N(Tf)}_2]$ than in $[\text{bmpy}][\text{OTf}]$. This suggests that the nitrating agent is more "reactive" in the former ionic liquid than in the latter.

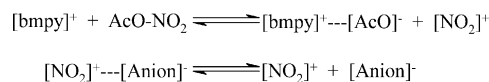
We can extend the discussion further. In our earlier work, we proposed that, although acetyl nitrate is generally regarded as a molecular nitrating agent, the solvent environment might give rise to dissociation of this molecule and subsequent formation of the nitronium ion, as illustrated in eqn. (1) below.



The nitronium ion thus generated would be a more potent nitrating agent than acetyl nitrate, and therefore explains the nitration of the deactivated aromatics in the ionic liquids.

The difference in yields in the two ionic liquids can also be explained. The effect of the cation and anion on solvent properties is now beginning to be understood. In this discussion we will focus on the hydrogen bonding properties of the ionic liquids, as determined by use of Kamlet-Taft parameters.²¹ It has been shown that the hydrogen bond donor property of an ionic liquid is largely affected by the cation (with some anion effect), whilst the hydrogen bond acceptor property is affected by the anion. Taking the two ionic liquids used in this work, because they are both based on the $[\text{bmpy}]^+$ cation they have similar *a* values. The ability of such cations to act as H-bond donors (through the hydrogen atoms on carbon atoms adjacent to a quaternary nitrogen) has already been demonstrated.²²

However, these $[\text{bmpy}]^+$ ionic liquids have different β values; 0.252 and 0.461 for the $[\text{N(Tf)}_2]^-$ and $[\text{OTf}]^-$ ionic liquids respectively.²³ These β values reveal that the triflate ionic liquid is the stronger H-bond acceptor solvent. This also means that the triflate anion will be more strongly coordinated to the ionic liquid cation (as revealed by the lower *a* value of this ionic liquid compared to the $[\text{N(Tf)}_2]^-$ version). This gives rise to two complementary effects. The first is that $[\text{bmpy}]^+$ is a more effective H-bond donor when coupled with the $[\text{N(Tf)}_2]^-$ anion, and so will be better able to coordinate (and cleave) acetate from acetyl nitrate. The second is that because $[\text{N(Tf)}_2]^-$ is the weaker base of the two anions used, it will coordinate the nitronium ion less strongly than $[\text{OTf}]^-$ will, thus leaving the nitronium ion more available to react in $[\text{bmpy}][\text{N(Tf)}_2]$ than in $[\text{bmpy}][\text{OTf}]$. These processes are illustrated in Scheme 2, and are consistent with the data reported in Table 1.



Scheme 2

Additionally we examined the nitration of the same substrates in $[\text{bmpy}][\text{N(Tf)}_2]$ using nitronium tetrafluoroborate under analogous conditions. Using this reagent, the effective nitrating agent is necessarily the nitronium ion. It was found that nitronium tetrafluoroborate is poorly soluble in this ionic liquid, but that as the reaction proceeds the suspension clears as the solid is consumed. The yields of nitroaromatics using the activated substrates were low, but this is not surprising given that the reactions were being conducted at 25 °C. Extensive decomposition of the aromatic (though not of the ionic liquid) was observed in these cases. However, the nitration of the deactivated substrates by nitronium tetrafluoroborate gave comparable yields and regioselectivities to those observed when using acetyl nitrate.

Table 1 Nitration of aromatic substrates by acetyl nitrate in dichloromethane, $[\text{bmpy}][\text{N(Tf)}_2]$ and $[\text{bmpy}][\text{OTf}]$ and a comparison with nitration by nitronium tetrafluoroborate in $[\text{bmpy}][\text{N(Tf)}_2]$. Yields after 1 h at 25 °C^a

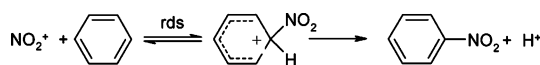
Substrate	Ac ₂ O/HNO ₃		[NO ₂][BF ₄]					
	CH ₂ Cl ₂		[bmpy][N(Tf) ₂]		[bmpy][OTf]		[bmpy][N(Tf) ₂]	
	Yield (%)	Ratio <i>o/p</i>	Yield (%)	Ratio <i>o/p</i>	Yield (%)	Ratio <i>o/p</i>	Yield (%)	Ratio <i>o/p</i>
Toluene	61	1.5	70	1.6	66	1.7	57 ^b	1.4
Mesitylene	45	—	89	—	80	—	28 ^b	—
Anisole	52	3	66	1.8	64	2.5	24 ^b	1.1
Chlorobenzene	0	—	64	0.29	8	0.17	54	0.20
Bromobenzene	0	—	59	0.33	7	0.28	57	0.37
2-Nitrotoluene	0 ^c	—	30 ^c	0.56 ^d	3 ^c	— ^e	38 ^c	0.56 ^d
Nitrobenzene	—	—	<1 ^c	<i>m</i> only	<1 ^c	<i>m</i> only	1 ^c	<i>m</i> only

^a All reactions in ionic liquids were heterogeneous, except where chlorobenzene and bromobenzene were used as substrates. ^b Decomposition observed.

^c 24 h. ^d 2,6-Dinitrotoluene/2,4-dinitrotoluene. ^e 2,4-Dinitrotoluene only.

These results support our earlier suggestion that, in ionic liquids, acetyl nitrate gives rise to nitronium ion, and that this is the effective nitrating agent in this system.

The effect of the anion has been investigated by choosing two which show very different hydrogen bond acceptor properties. It has been demonstrated that the ionic liquid which is the poorest H-bond acceptor ($[N(Tf)_2]^-$) is the best suited for aromatic nitrations because it does not coordinate the electrophile as strongly as the triflate anion can. In a reaction such as this, where the rate determining step is normally the formation of the Wheland intermediate (Scheme 3), the solvent which binds the electrophile least strongly will give the highest yield after unit time. Given that β is largely anion dependent, even if other common anions had been available to us, it is worth noting that $[BF_4]^-$ is a stronger H-bond acceptor, whilst $[PF_6]^-$ is comparable, if slightly weaker, and that only $[SbF_6]^-$ is a significantly weaker H-bond acceptor.²¹ Given that $[PF_6]^-$ readily evolves F^- (as HF) and that $[SbF_6]^-$ might be expected to behave similarly, these alternatives are not attractive.



Scheme 3

Whilst we have not completely excluded the possibility that acetyl nitrate is capable of acting as a molecular nitrating agent in the ionic liquid, the evidence to date from our studies does not suggest that acetyl nitrate acts as a molecular nitrating agent in ionic liquids.

It is instructive to compare the nature of the intermediate of this reaction with the transition state formed in electrophilic bromination by $[Br_3]^-$ in ionic liquids (Fig. 2).²⁰ In the bromination reactions, the $[Br_3]^-$ ion dissociates to form bromine and bromide. Bromine then attacks the double bond and this complex is then attacked by Br^- . Therefore, in the bromination reaction, as one bromide---cation bond is broken, so another is formed. This suggests that the identity of the ionic liquid will have very little effect on this part of the reaction (since each cation---bromide adduct will have identical bond strength).

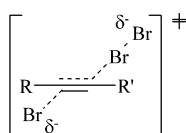


Fig. 2 Transition state of electrophilic bromination by $[Br_3]^-$.

This contrasts with nitration, where the rate-determining step is attack of the substrate by the nitronium ion. The identity of the ionic liquid will affect the rate of this step because the interactions (this time of the anion with either the nitronium ion or with the Wheland intermediate) will not be of equal strength. So far we have only been able to consider the effect of the ionic liquid on its interactions with the nitronium ion. We can only speculate about any interactions between the ionic liquid and the Wheland intermediate.

Kinetic studies of aromatic nitrations

Kinetic studies of the aromatic nitrations were attempted in $[bmpy][N(Tf)_2]$ and in dichloromethane. An excess of substrate relative to acetyl nitrate was used in the hope of obtaining *pseudo* first order kinetics. However, the reactions did not obey a simple model and it proved impossible to obtain a satisfactory fit of the data. For this reason, it was decided to make a study of the initial rates of reaction. In this work, the effect of both nitric acid concentration and acetic anhydride concentration was investigated.

Chlorobenzene is completely soluble in $[bmpy][N(Tf)_2]$ and reacts slowly enough to be conveniently sampled and quantified. Thus we chose this as a model substrate for nitration in the ionic

liquid. In dichloromethane we studied nitration under analogous conditions, but used toluene as substrate (chlorobenzene being unreactive in this solvent). It was assumed that the reaction would be first order in $[substrate]$ in both solvents. Where the substrate is particularly activated, a zeroth order dependence on $[substrate]_0$ can be observed, but the reaction of toluene with $AcONO_2$ normally shows first order dependence on $[toluene]$.²⁴

It is known that, depending on the reaction conditions, nitrations by acetyl nitrate in acetic anhydride show a dependence on $[HNO_3]_0$ which is between 2nd and 3rd order. The order depends on $[HNO_3]_0$, with lower concentration leading to 3rd order and higher concentration leading to 2nd order dependence on $[HNO_3]_0$.²⁴

In this work we found that, in both the ionic liquid and in dichloromethane, the order of reaction with respect to $[HNO_3]$ was between 2 and 3. This observation is in accord with nitration by nitric acid in acetic anhydride, even if the reactions are not necessarily by acetyl nitrate in both solvents studied in this work.

Attempts were made to establish the effect of $[Ac_2O]_0$ concentration on the rate law, and determine the order of reaction with respect to this reagent, but these were inconclusive, save to suggest that the reaction is of high order with respect to the concentration of acetic anhydride in both solvents.

Recycling the ionic liquid

Before ionic liquids are adopted as solvents for the production of nitroaromatics, a regime by which the solvent may be recovered and re-used must be developed. A possible means of achieving this is described here. For ease of handling, the reactions were performed on a larger scale, starting with 4 cm³ of ionic liquid. However, the reaction was carried out using the same proportions of reagent, substrate and solvent as in the other reactions. Chlorobenzene was chosen as the substrate because it was anticipated that the reaction would not go to completion within the reaction time, allowing us to observe whether the yield after unit time (which gives an idea of the rate, although is not equal to it) was affected. The ionic liquid chosen was $[bmpy][N(Tf)_2]$, which is immiscible in water.

Recycling of the ionic liquid was achieved by dissolving the post-reaction mixture into dichloromethane and adding water. It was then possible to extract any unreacted nitric acid, plus the acetic acid generated by reaction with water. After removing the dichloromethane, the organics were removed from the ionic liquid by steam distillation, extracted from the water with dichloromethane and rotary evaporated to remove the solvent and substrate. This gave the product as a mixture of the 2- and 4- isomers of chloronitrobenzene; the ratio was determined by GC. Meanwhile, the ionic liquid was recovered by extracting with dichloromethane and then heating *in vacuo*. This process is illustrated in Fig. 3. A sample of the ionic liquid was withdrawn after each run, and before it was reused it was analysed by ¹H NMR spectroscopy. This revealed that there was no difference between the recovered ionic liquid and the original.

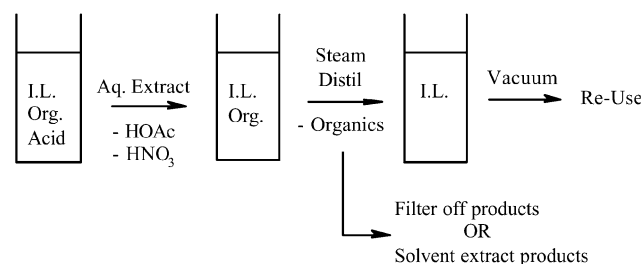


Fig. 3 Schematic representation of the ionic liquid recycling process.

The results of the nitrations are shown in Table 2, as are data to show the amount of ionic liquid recovered after each reaction (after removal of the sample for NMR analysis).

Table 2 Nitration of chlorobenzene and recycling of [bm₂py][N(Tf)₂] ionic liquid

Run	Yield (%)	Ratio <i>o/p</i>	Mass of ionic liquid recovered ^a /g
1	76	0.26	5.23
2	70	0.24	5.15
3	71	0.25	5.07
4	76	0.24	4.83
5	74	0.24	4.57

^a Initial mass of ionic liquid 5.45 g (ca. 4 cm³).

It is clear that there is one major problem with the recycling of the ionic liquid as described above; the reliance on dichloromethane does not make this process appear green at first glance. It should be stated that the role of dichloromethane in this work was to enable the determination of both product and recovery of the ionic liquid. In an industrial setting, it would be quite possible to perform a steam distillation of the entire reaction mixture. The organics will form a separate phase from the aqueous acids distilled and could probably be removed by simple decantation. And because this ionic liquid ([bm₂py][N(Tf)₂]) is immiscible in water, it should be possible to decant any water from the ionic liquid and re-use it immediately. Thus recycling the ionic liquid does not require the use of dichloromethane.

Table 2 does show a steady loss of ionic liquid after each run. There was no degradation of the ionic liquid during the reaction, as evidenced by the NMR spectra of the ionic liquid after each run and the fact that there was no discolouration. Therefore it is reasonable to propose that these losses are purely mechanical, arising from the washing procedure employed.

Conclusions

This work has clearly shown that there is potential for ionic liquids to be used to achieve nitrations of even quite deactivated compounds at ambient temperatures using only a stoichiometric amount of nitric acid and without the use of excess (or indeed any) sulfuric acid.

Acetyl nitrate is a more potent nitrating agent in ionic liquids than in molecular solvents. This is because acetyl nitrate dissociates to form nitronium acetate in the ionic liquid and it is therefore the nitronium ion which is the effective nitrating agent in this system. The importance of knowing the mechanism of a given reaction in order to inform our decision of which solvent to use has also been demonstrated. In examples of electrophilic substitutions where the rate-determining step is the addition of the electrophile, the solvent of choice should be a weaker hydrogen bond acceptor. The study of the kinetics of nitrations in ionic liquids reveals that the dependence of rate upon nitric acid concentration is similar to that observed when the same reactions are conducted in acetic anhydride. Further study of the kinetics will be made and will form another part of this study.

Finally, it has been shown that the ionic liquids can be recycled and reused for aromatic nitrations. The losses of ionic liquid were mainly mechanical (including withdrawal of a sample for nmr from each run). These can be overcome by a combination of working on a larger scale and of not removing the ionic liquid from the reaction vessel between each run.

Experimental

The ionic liquids were prepared and purified as described elsewhere.²⁵ Dichloromethane was distilled prior to use. All of the nitrations were conducted at 25 °C under a nitrogen atmosphere using standard Schlenk techniques. All substrates and reagents purchased were used as received.

Nitration by acetyl nitrate

To the ionic liquid (1 cm³) was added a known mass of nitric acid (70% w/w, ca. 0.03 cm³, 0.6 mmol), acetic anhydride (0.25 cm³)

and hexadecane. At a known time the substrate (1 cm³) was added and the mixture stirred for 1 h before sampling.

Nitration by nitronium tetrafluoroborate

A portion of nitronium tetrafluoroborate (0.08 g, 0.6 mmol) was added to a tared Schlenk flask in a dry nitrogen atmosphere glovebox. The sealed flask was removed from the glovebox and to it was added [bm₂py][N(Tf)₂] (1 cm³) and hexadecane. At a known time the substrate (1 cm³) was added and the mixture stirred for 1 h before sampling.

Recycling

The reactions were conducted by a method analogous to that described for the acetyl nitrate nitrations, but using four times the quantities for ease of handling.

After 1 h, the reaction mixture was added to water (100 cm³) and rinsed in with dichloromethane (4 × 5 cm³). The ionic liquid and organics were removed, and the aqueous phase was extracted with dichloromethane (4 × 20 cm³). The combined dichloromethane phase was combined and the solvent removed *in vacuo*. The organics were removed from the ionic liquid by steam distillation, isolated by extraction with dichloromethane (4 × 10 cm³) from the aqueous phase and evaporated to constant mass, yielding a mixture of chloro-2-nitrobenzenes and chloro-4-nitrobenzenes. The ratio was determined by GC-MS.

Likewise, the ionic liquid was extracted from the aqueous phase using dichloromethane (4 × 10 cm³) and heated under high vacuum to constant mass. The ¹H NMR spectrum of the recovered ionic liquid was identical to that of the original, with no evidence of impurities.

The recovery of the ionic liquid and the yields of each reaction are documented in Table 2.

Sampling

Except in the recycling study (where the product was isolated) the reactions were monitored by taking samples at a known time, which were then quenched into saturated sodium bicarbonate solution and extracted with dichloromethane. Analysis was by GC-MS using hexadecane as an internal standard. Retention times were determined by using authentic samples of the nitroaromatics. Note that where the reaction mixture was not homogeneous, then the entire reaction mixture was quenched and extracted as described above.

Acknowledgements

Thanks go to Mr Andy Cakebread and Mr Roger Tye (King's College London) for performing GC-MS analyses.

References

- 1 N. L. Lancaster and V. Llopis Mestre, *Chem. Commun.*, 2003, 2812.
- 2 (a) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (b) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (c) R. Sheldon, *Chem. Commun.*, 2001, 2399; (d) C. M. Gordon, *Appl. Catal. A*, 2001, **222**, 101; (e) H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A: Chem.*, 2002, **182**, 419; (f) D. Zhao, M. Wu, Y. Kou and E. Min, *Catal. Today*, 2002, **74**, 157.
- 3 *Ionic Liquids in Synthesis*, eds. T. Welton and P. Wasserscheid, Wiley-VCH, Weinheim, 2002.
- 4 For a review of the solvent properties of ionic liquids, see: C. F. Poole, *J. Chromatogr. A*, 2004, **1037**, 49.
- 5 A. Cornelis, L. Delaude, A. Gerstmanns and P. Laszlo, *Tetrahedron Lett.*, 1988, **29**, 5909.
- 6 B. M. Choudary, M. Ravichandra Sarma and K. Vijaya Kumar, *J. Mol. Catal.*, 1994, **87**, 33.
- 7 (a) R. P. Claridge, N. L. Lancaster, R. W. Millar, R. B. Moodie and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1815; (b) R. P. Claridge, N. L. Lancaster, R. W. Millar, R. B. Moodie and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 2001, 197.
- 8 (a) K. Smith, S. Almeer and C. Peters, *Chem. Commun.*, 2001, 2748; (b) K. Smith, T. Gibbins, R. W. Millar and R. P. Claridge, *J. Chem.*

- Soc., Perkin Trans. 1*, 2000, 2753; (c) K. Smith, A. Musson and G. A. DeBoos, *J. Org. Chem.*, 1998, **63**, 8448.
- 9 (a) D. Vassena, A. Kogelbauer and R. Prins, *Catal. Today*, 2000, **60**, 275; (b) M. Haouas, S. Bernasconi, A. Kogelbauer and R. Prins, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5067; (c) S. Bernasconi, G. D. Pirngruber, A. Kogelbauer and R. Prins, *J. Catal.*, 2003, **219**, 231; (d) S. Bernasconi, G. D. Pirngruber and R. Prins, *J. Catal.*, 2004, **224**, 297.
- 10 F. J. Waller, A. G. M. Barrett, D. C. Braddock, R. M. McKinnell and D. Ramprasad, *J. Chem. Soc., Perkin Trans. 1*, 1999, 867.
- 11 T. N. Parac-Vogt and K. Binnemans, *Tetrahedron Lett.*, 2004, **45**, 3137.
- 12 R. R. Bak and A. J. Smallridge, *Tetrahedron Lett.*, 2001, **42**, 6767.
- 13 A. J. Hill, R. W. Millar and J. P. B. Sandall, *Org. Biomol. Chem.*, 2004, **2**, 90.
- 14 (a) M. R. Crampton, L. M. Gibbons and R. W. Millar, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1662; (b) M. R. Crampton, E. L. Cropper, L. M. Gibbons and R. W. Millar, *Green Chem.*, 2002, **4**, 275.
- 15 (a) K. Schofield, *Aromatic Nitration*, Cambridge University Press, Cambridge, 1980; (b) G. Olah, R. Malhotra and S. C. Narang, *Nitration: Methods and Mechanisms*, VCH, New York, 1989.
- 16 K. K. Laali and V. J. Gettwert, *J. Org. Chem.*, 2001, **66**, 35.
- 17 M. J. Earle, S. P. Katdare and K. R. Seddon, *Org. Lett.*, 2004, **6**, 707.
- 18 K. Qiao and C. Yokoyama, *Chem. Lett.*, 2004, **33**, 808.
- 19 R. Rajagopal and K. V. Srinivasan, *Synth. Commun.*, 2003, **33**, 961.
- 20 (a) C. Chiappe, V. Conte and D. Pieraccini, *Eur. J. Org. Chem.*, 2002, 2831; (b) O. Bortolini, M. Bottai, C. Chiappe, V. Conte and D. Pieraccini, *Green Chem.*, 2002, **4**, 621; (c) C. Chiappe, D. Capraro, V. Conte and D. Pieraccini, *Org. Lett.*, 2001, **3**, 1061.
- 21 (a) C. P. Fredlake, M. J. Muldoon, S. N. V. K. Sudhir, T. Welton and J. F. Brennecke, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3280; (b) L. Crowhurst, P. R. Mawdsley, J. M. Pérez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.
- 22 L. Crowhurst, N. L. Lancaster, J. M. Pérez Arlandis and T. Welton, *J. Am. Chem. Soc.*, 2004, **126**, 11549.
- 23 C. E. Cannizzaro and K. N. Houk, *J. Am. Chem. Soc.*, 2002, **124**, 7163.
- 24 See ref. 15a, pp. 63–64.
- 25 N. L. Lancaster, P. A. Salter, T. Welton and G. B. Young, *J. Org. Chem.*, 2002, **67**, 8855. See also Supporting Information from ref. 23.